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## Do you know where your Humic Acids Come From?

### Whence Comest Your Humic Acids?

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Numerous articles within the past five years have given the particulars of the wherefores of organic acids. The dilemma when purchasing humic acid (HA) and (FA) products should revolve around both guaranteed percents and parent material. There are numerous descriptive terms and definitions of all things humic that can be a confusing. Ultimately, one must decide on a preferred term or definition and stick to it. This article will select its own preferences and use same throughout the discourse.

**Humate Geologically**, is weathered lignite, weathered coal and carbonaceous material that contains humic matter (primarily HA and FA) (Hoffman et al., 1996)

**Humic Matter** Completely decomposed organic matter containing humic acid (S Waddell, 1968)

**Humic Acids (HAs)** Humic and fulvic acids (Siemers and Waddell, 1972)

**Humic Acid (HA)** Base-soluble humic substance insoluble in acid conditions (be Aiken et al., 1985)

**Fulvic Acid (FA)** Fraction of humic substances soluble (in water under all pH conditions) (Aiken et al., 1985)

**Humic Fraction** of humic substances not soluble in water at any pH value (Aiken 1985)

Carbonaceous Mudstone Humate if it contains base-soluble humic acid (Siemers Waddell, 1977)

**Weathered Coal** Oxidized coal that contains humic acids due to - weathering process (Roybal and Barker, 1987)

**Weathered Lignite** True leonardite (Siemers and Waddell, 1977)

**Fresh Coal** Before weathering and contains little or no humic acid (Hoffman et al)

**Lignite** A soft coal intermediate between peat and bituminous coal (Miles and Bl

Peat Partially decomposed organic matter (2.8 - 4.0 pH) preserved under anaerobic conditions (Davis, 1985)

- Humates occur geologically in horizontal lenses often interbedded with fresh coal mudstone. The lenses are mined with front-end loaders, stacked to dry, screened, bagged. From a quality stand point, it is difficult to maintain guaranteed percent pulling material from a single source on any given day along any given humate source.

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• Humate beds/seams can range from 2 percent to 80 percent HA, depending on the clay mineral content. These clays are typically illite, kaolinite and smectite.

• Three different categories of humic material (humate) are leonardite (weathered lignite), carbonaceous mudstone and weathered coal.

• Fresh coal is high in calorific value (heat), but low in humic acid content. Sulfide sulfurs will indicate the lack of weathering.

• Carbonaceous mudstone has more clay than weathered coal, thereby being more beneficial in sandy soils for retaining nutrients and moisture. A clay-dominant soil would receive more benefit from weathered, coal-based humates (leonardite, weathered coal) because of their base-soluble, humic acid content.

• The average humic acid content varies - in weathered coal 66 percent; leonardite, up to 80 percent; carbonaceous mudstone 11 percent; and fresh coal about 10 percent.

• Two basic methods of humic acid analyses are the California Method (CALIF 4A/JC) and the Colormetric method (COM SSPA 15(12)84). Generally, if a number using the California Method is doubled, a Colormetric Method number will be realized, i.e., 4.75 percent X 2 = 9.5 percent

• Most humic acids have guarantees that range from 1-65 percent. Labeling in the State of California (CDFA) demands the California Method - all other states will accept the Colormetric Method.

• Dry humates will typically carry high HA and/or FA percentages, especially if not reported on an ash-free basis.

• Liquid humic add products can range from 1-20 percent. Liquids above 4-5 percent humic acid will have a tendency to settle out.

• When purchasing HAs and FA's ask for a guaranteed percent and an analysis sheet from a third party laboratory that uses the California Method of HA analysis. A guaranteed FA percent is more difficult as it is almost impossible to find a laboratory that will do this analysis. Ask your salesperson how their product is guaranteed.

• When choosing HAs ask the genesis of the parent humate - carbonaceous mudstone = good; weathered coal = better; leonardite - best.

• Good humic acid products would be those that pull material from several different sources for diversity of humic acid and fulvic acid content, organic-rich day content and microorganisms.

• Black as coal with an earthy-coal odor, looking and feeling slightly oily and no hint of ammonia are indicators of a quality liquid humic acid product-

• Microorganisms inhabiting raw humates can include yeasts, molds, bacteria and actinomycetes. A soft or cold humic acid extraction method (not utilizing potassium hydroxide and HCl) will allow numerous species to survive and be available for inoculation of soils receiving a liquid humic add product.

• HAs are extremely complex, variable organic molecules the exact structure of which are unknown.

• Every molecule of HA and FA can be different yet have similar properties when related to the individual entities present in any particular microenvironment. The possibilities for reactions or combinations are limitless.

• Humic adds are organic colloids, behaving somewhat like clays, thus increasing the water-retention capacity of soil.

• Decomposition of rocks and minerals to form soil and in turn increasing the workability of

soil is promoted by HAs.

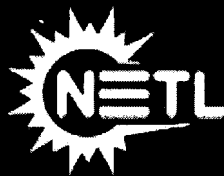
- The acidity of alkali soil is increased with the use of HAs, thereby making several more available to plants and stimulating growth and proliferation of microorganisms that process plant nutrients.

In summary: Be curious about the organic acids you are purchasing. Try not to let selections be cost driven, and remember that there are two different kinds of common sense - commonsense and nonsense.

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## Foreword

The Morgantown Energy Technology Center (METC) sponsored and hosted the conference on Industry Partnerships to Deploy Environmental Technology on October 22-24, 1996, in Morgantown, West Virginia.

METC became part of the Federal Energy Technology Center (FETC) on December 2, 1996, with the

consolidation of METC and the Pittsburgh Energy Technology Center (PETC). The new unified Center research partners and stakeholders the combined resources of two world-class research centers while at the same time, meeting the Department of Energy's commitment to reducing costs and improving the efficiency of energy and environmental programs.

Three goals were accomplished at the meeting: review of the latest environmental and waste-management technologies being developed under FETC sponsorship; addressing the accomplishments in, and barriers to, affecting, private-sector development of these technologies; and laying the groundwork for future technology development initiatives and opportunities.

Almost 275 attendees from industry, academia, national laboratories, DOE, and other Government agencies participated in the 3-day conference. The agenda format was 36 papers and 32 poster presentation sessions, two poster sessions, and a panel discussion. The opening session included the projected potential for environmental technologies. Topics covered in the five remaining formal sessions were focus area, subsurface contaminants, high-level waste-remediation-tanks focus area, technical base development, and decontamination and decommissioning focus area. The panel discussion was on programs that support the various focus areas.

The papers and presentations in this document were produced primarily from electronic files provided by the authors. They have been neither refereed nor extensively edited. The conference Proceedings were made available to participants on a CD-ROM, and is also available as paper copy or microfiche from the Office of Scientific and Technical Information, or as microfiche or blowback from microfiche from the National Technical Information Service. The papers and presentations are available worldwide on the FETC-Morgantown Homepages on the internet (URL: <http://www.netl.doe.gov>).

#### **Conference Technical Team**

Vijendra P. Kothari  
C. Edward Christie  
Clifford P. Carpenter

#### **Session 1 — Opening Session**

##### *Overcoming Obstacles in Environmental Partnerships: Validation of Technology Performance*

Claire H. Sink — U.S. Department of Energy; and  
Stanley Chanesman — U.S. Department of Commerce

##### *Human Factors Assessments of Environmental Technologies*

Donald R. Carson, B.P. Shagula, and John B. Moran — Operating Engineers National HAZ Program

##### *Efficacy Testing of Environmental Technology*

M.A. Ebadian — Hemispheric Center for Environmental Technology

##### *The Environmental Technology Leveraging Initiative*

S.A. Meacham — Global Environment & Technology Foundation; and  
K.D. Pearce — Morgantown Energy Technology Center

#### **Session 2A — Mixed Waste Focus Area**

##### *Innovative Vitrification Technology for Soil Remediation*

James G. Hnat, John S. Patten, and Norman W. Jetta — Vortec Corporation

##### *Application of Catalytic Extraction Processing to DOE Wastes*

J. Zimmerman — Molten Metal Technology, Inc.

Development Studies of a Novel Wet Oxidation Process

Terry W. Rogers and Patrick M. Dhooge — *Delphi Research, Inc.*

Waste Inspection Tomography (WIT)

Richard T. Bernardi — *Bio-Imaging Research, Inc.*

Steam Reforming of Low-Level Mixed Waste

Gary E. Voelker and William G. Steedman — *ThermoChem, Inc.*; and  
Ravi R. Chandran — *Manufacturing and Technology Conversion International, Inc.*

An Intelligent Inspection and Survey Robot

Joseph S. Byrd — *University of South Carolina*

Performance Evaluation of an Autonomous Hazardous Waste Inspection Vehicle

Eric Byler — *Lockheed Martin Astronautics*

**Session 2B — Subsurface Contaminants**

Subsurface Contaminants Focus Area Perspective

James Wright — *DOE Savannah River Operations Office*

Surfactant-Enhanced Aquifer Remediation at the Portsmouth Gaseous Diffusion Plant

Richard E. Jackson, Minquan Jin, John T. Londergan, John F. Pickens, and Carl M. Young  
*Inc.*;  
John C. Fountain, Nicole Case, and Alison Lagowski — *State University of New York at Bui*  
Gary A. Pope — *University of Texas at Austin*

Barometric Pumping with a Twist: VOC Containment and Remediation without Boreholes

William Lowry, Sandra Dalvit Dunn, and Donald Neeper — *Science & Engineering Associat*

Steerable/Distance Enhanced Penetrometer Delivery System

Ali Amini and Gregory M. Boyd — *UTD Incorporated*

Measuring Fuel Contamination Using Cone Penetration Testing and High Speed Gas Chromatogra

Wesley L. Bratton and Stephen P. Farrington — *Applied Research Associates, Inc.*; and  
Michael Akard — *Chromatofast, Inc.*

Road Transportable Analytical Laboratory (RTAL) System

Stanley M. Finger — *Engineering Computer Optecnomics, Inc.*

Field-Usable Portable Analyzer for Chlorinated Organic Compounds

William J. Buttner, William R. Penrose, and Joseph R. Stetter — *Transducer Research, Inc.*  
Roger D. Williams — *TSI Incorporated*

Field Portable Detection of Hazardous Compounds Using a SAW/GC System

Edward J. Staples and George A. Pappas — *Amerasia Technology Inc.*

**Session 3A — High-Level Waste-Remediation Tanks Focus Area**

High-Level Waste Remediation Tanks Focus Area Perspective

Billie Mauss — *DOE Richlands Operations Office*

Houdini<sup>TM</sup>: A Remote Mobile Platform for Tank Waste Retrieval Tasks

Tim J. Denmeade, Adam D. Slifko, Bruce R. Thompson, and David W. White — *RedZone F*

*A Fly-by Robotic Tank Inspection End-Effector for Waste Storage Tank*

Mark M. Gittleman, Bill Robertson, Ben Lee, Tom Gaseor, and Bill Wightman — Oceaneering Systems; and  
Gregory Hughes — Oceaneering International, Incorporated

*An Advanced Open Path Atmospheric Pollution Monitor for Large Areas*

L. Taylor, D. Suhre, S. Mani, T. Oblak, J. Ranka, and J. Seidel — Northrop Grumman STC;  
M. Myers and R. Pollard — Northrop Grumman EOSS;  
R. Anderson — Westinghouse STC; and  
B. McVey, G. Busch, R. Nemzek, and M. Schmitt — Los Alamos National Laboratory

**Session 3B — Technical Base Development**

*Hemispheric Center for Environmental Technologies Research & Development Capabilities*

Joseph F. Boudreaux — Florida International University

*Technologies Development for Environmental Restoration and Waste Management: International University & Research Institution and Industry Partnerships*

Roy C. Herndon, John E. Moerlins, and J. Michael Kuperberg — Florida State University

*WVU Cooperative Agreement, Decontamination Systems Information & Research Program, Deploy Leading to Implementation*

Echol E. Cook — West Virginia University

*Environmental Management Technology Demonstration and Commercialization Under the METC-E Cooperative Agreement*

Edward N. Steadman, Daniel J. Daly, Ames A. Grisanti, John R. Gallagher, Gerald H. Groer, Steven B. Hawthorne, John P. Hurley, Robert O. Ness, Everett A. Sondreal, and Daniel J. S Energy and Environmental Research Center, University of North Dakota

*Tulane/Xavier Center for Bioenvironmental Research Project, Hazardous Materials in Aquatic Envir Subproject: Biomarkers and Risk Assessment in Bayou Trepagnier, LA*

C. Ide — Tulane University

**Session 4 — Decontamination & Decommissioning Focus Area**

*Rosie: Remote Work System for Decontamination and Dismantlement*

Leona C. Bares, Louis S. Conley, and Bruce R. Thompson — RedZone Robotics, Inc.

*Characterization of Pipes, Drain Lines, and Ducts using the Pipe Explorer™ System*

C. David Cremer, D.T. Kendrick, and Eric Cramer — Science and Engineering Associates, .

*Electrokinetic Decontamination of Concrete*

Henry L. Lomasney, Ashoke K. SenGupta, and Valeriy Yachmenev — ISOTRON Corporati

*Field Testing of the Advanced Worker Protection System*

Richard J.E. Todd and Doris Hamill — Oceaneering Space Systems

*Advanced Technologies for Decontamination and Conversion of Scrap Metal*

Valerie MacNair, Thomas Muth, Kenneth Shasteen, and Alan Liby — Manufacturing Scienc Corporation;  
George Hradil — Covofinish Co.; and  
Brajendra Mishra — Colorado School of Mines

The ROVCO<sub>2</sub> Surface Decontamination System

Andrew M. Resnick, Michele Reed, and Odoardo Lopez-Yanes — *Oceaneering International*

BOA II: Pipe-Asbestos Insulation Removal Robot System

H. Schempf, E. Mutschler, S. Boehmke, B. Chemel, and C. Piepgras — *Robotics Institute, Carnegie Mellon University*

**Poster Session I**

Novel Silica-Based Ion Exchange Resin

M. Gula and J. Harvey — *Eichrom Industries, Inc.*

Radionuclide Capture Using Membranes

Lloyd R. White, Thomas M. Kafka, Keith M. Hoffman, and Robert D. Topness — *3M Company*

Membrane System for Recovery of Volatile Organic Compounds from Remediation Off-Gases

J.G. Wijmans, S.K. Goakey, and R.W. Baker — *Membrane Technology and Research, Inc.*

Measurement of Radionuclides Using Ion Chromatography and Flow-Cell Scintillation Counting With Shape Discrimination

T.A. DeVol, R.A. Fjeld, and J.E. Roane — *Clemson University*;  
J.D. Leyba — *Westinghouse Savannah River Corporation*; and  
S.D. Branton — *U.S. Nuclear Regulatory Commission*

Acoustically Enhanced Remediation, Phase II — Technology Scaling

Joe L. Iovenitti and Donald G. Hill — *Weiss Associates*;  
Timothy M. Rynne, John F. Spadaro, and William Hutchinson — *Scientific Applications and Associates, Inc.*; and  
Tissa Illangasakere — *University of Colorado*

Fiber Optic/Cone Penetrometer System for Subsurface Heavy Metals Detection

Steven Saggese — *Science & Engineering Associates, Inc.*; and  
Wes Bratton and Bryan Fisk — *Applied Research Associates, Inc.*

Surfactant-Altered Zeolites as Permeable Barriers for In Situ Treatment of Contaminated Groundwater

Robert S. Bowman — *New Mexico Tech*

Internal Reflection Sensor for the Cone Penetrometer

John W. Haas III, Thomas M. Johnston, and R. David Rath — *EIC Laboratories, Inc.*

Laboratory Test Results of an On-Line Real-Time Alpha Radiation Measuring Instrument for Liquid

Keith D. Patch, Frederick E. Becker, and Steven N. Bittenson — *Thermo Power Corporation Division*

The LASI High-Frequency Electromagnetic Subsurface-Imaging System, System Description and D Site-Characterization Survey at the Idaho National Engineering Laboratory

Ben K. Sternberg and Mary M. Poulton — *Laboratory for Advanced Subsurface Imaging (LASI), University of Arizona*

Development of HUMASORB<sup>TM</sup>, A Lignite Derived Humic Acid for Removal of Metals and Organic Contaminants from Groundwater

H.G. Sanjay, M. Tiedje, J.J. Stashick, K.C. Srivastava, H.R. Johnson, and D.S. Walia — *AFRL*

Organic Sponges for Cost Effective CVOC Abatement

Patricia D. Mackenzie, Timothy M. Sivavec, Marsha M. Grade, David P. Horney, and Joseph J. GE Corporate Research and Development Center



Progress of Electro-Hydraulic Scabbing Technology for Concrete Decontamination

V. Goldfarb and R. Gannon — *Textron Systems Division*

**Poster Session II**

Electromagnetic Mixed Waste Processing System for Asbestos Decontamination

Raymond S. Kasevich and Walter Vaux — *KAI Technologies, Inc.*;  
Nancy Ulerich — *Westinghouse Science & Technology Center*; and  
Tony Nocito — *Ohio DSI Corporation*

Fiber Optic Coherent Laser Radar 3D Vision System

Robert B. Clark, Philip G. Gallman, and Anthony R. Slotwinski — *Coleman Research Corp*  
Kelvin Wagner, Sam Weaver, and Jieping Xu — *University of Colorado*

Diagnostics and Data Fusion of Robotic Sensors

M. Dhar, S. Bardsley, L. Cowper, R. Gamache, R. Hamm, V. Jammu, and J. Wagner — *Me Technology Incorporated*

Protective Clothing Based on Permselective Membrane and Carbon Adsorption

D.L. Gottschlich, J.G. Wijmans, and R.W. Baker — *Membrane Technology and Research, I*

Laser Surface Cleaning

Eric C. Crivella, Joyce Freiwald, and David A. Freiwald — *F2 Associates Inc.*

Rapid Surface Sampling and Archival Record (RSSAR) System

E. Barren, S.B. Dorn, A.L. Ortiz, Jr., C.M. Penney, R.B. Sheldon, A.P. Shapiro, and A.A. Br  
*Corporate Research and Development*; and  
T.G. Albro, R.S. Marshall, and J.C.E. Berends, Jr. — *EAI Corporation*

Portable Sensor for Hazardous Waste

Lawrence G. Piper, Amy J.R. Hunter, Mark E. Fraser, and Steven J. Davis — *Physical Scie*

Three Dimensional Characterization and Archiving System

Robert Clark, Phillip Gallman, James Gaudreault, Richard Mosehauer, and Anthony Slotwir  
*Coleman Research Corporation*;  
George Jarvis — *Thermedics Detection, Inc.*; and  
Peter Griffiths — *University of Idaho*

RoboCon: Operator Interface for Robotic Applications

H. Schempf, J. Warwick, M. Fung, B. Chemel, and M. Blackwell — *Robotics Institute, Carn*  
*University*

Field-Scale Model for Air Sparging Performance Assessment and Design

G. Hein, N. Hutzler, and J. Gierke — *Michigan Technological University*; and  
R. Falta — *Clemson University*

Tomographic Site Characterization Using CPT, ERT and GPR

R. Morey — *Applied Research Associates, Inc.*

Field Raman Spectrograph for Environmental Analysis

John W. Haas III, James M. Sylvia, Michael M. Carrabba, and R. David Rauh — *EIC Labor*

Liquid Membrane System for the Removal and Concentration of Transuranic Elements

Mark R. Timmins, S. Ronald Wysk, Leo A. Smolensky, and Daming Jiang — *LSR Technolo*  
and

Gregg J. Lumetta — *Battelle, Pacific Northwest Laboratories*

*Automated Baseline Change Detection*

Peter A. Berardo, Carl Adams, and Bill Dickson — *Lockheed Martin Missiles & Space*; and  
Guy Immega, Jeremy Wilson, and Gloria Chow — *Kinetic Sciences, Inc.*

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**NOTE:** The abstracts/papers listed above are in Portable Document Format (PDF). To view PDF file necessary to first download and install the free [Adobe Acrobat Reader](#) from Adobe Systems, Inc. See [started instructions](#) for help.

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# **Development of HUMASORB™, A Lignite Derived Humic Acid for Removal of Metals and Organic Contaminants from Groundwater**

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14100 Park Meadow Drive, Suite 210  
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## **Introduction<sup>1</sup>**

Heavy metal and organic contamination of surface and groundwater is a major environmental concern. The contamination is primarily due to improperly disposed industrial wastes. Decontamination of surface and groundwater can be achieved using a broad spectrum of treatment options such as precipitation, ion-exchange, microbial digestion, membrane separation, activated carbon adsorption, etc. The state-of-the-art technologies for treatment of contaminated water, however, can in one pass remediate only one class of contaminants, i.e., either VOCs (activated carbon) or heavy metals (ion exchange). The groundwater contamination at different Department of Energy (DOE) sites (e.g., Hanford) is due to the presence of both VOCs and heavy metals. Therefore, two different stepwise processes are needed to remediate a site. The two-step approach increases the cost of remediation. A novel material having properties to remove both classes of contaminants in one step is being developed as part of this project.

## **Objective**

The objective of this project is to develop a lignite derived adsorbent, HUMASORB™, to remove heavy metal and organic contaminants from groundwater and surface water streams in one processing step. As part of this project, HUMASORB™ is being characterized and evaluated for its ion-exchange and adsorption capabilities.

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<sup>1</sup> Research sponsored by the U.S. Department of Energy's Morgantown Energy Technology Center, under Contract DE-AR21-95MC32114 with ARCTECH, Inc. 14100 Park Meadow Drive, Chantilly, VA 22021; telefax: 703-222-0299.

## **Approach**

This project is aimed at the development of HUMASORB™, an adsorbent having the unique properties of humic acid. Humic acid is a natural material with many properties which can be exploited for several cost effective applications. Humic substances are complex mixtures of naturally occurring organic materials. These substances are formed from the decay of plant and animal residues in the environment. Humic acid constitutes a significant portion of the acid radicals found in humic substances.

A major source of humic acid is coal-- the most abundant and predominant product of plant residue coalification. All ranks of coal contain humic acid but lignite represents the most easily available and concentrated form of humic acid. Humic acid concentration of lignite varies from 30-90 % depending on location. Peat, humates and sewage sludge also contain significant quantities of humic acid.

The properties of humic acid for chelation of metals and adsorption of organics were reviewed in an earlier report on this project (1). As discussed in that report, humic acid is dark brown to black in color. It is considered a complex aromatic macromolecule with various linkages between the aromatic groups. The different compounds involved in linkages include, amino acids, amino sugars, peptides, aliphatic acids and other aliphatic compounds. The various functional groups in humic acid include, carboxylic (COOH), phenolic, aliphatic and enolic - hydroxyl and carbonyl (C=O) structures of various types. Humic acid is an association of molecules forming aggregates of elongated bundles of fibers at low pHs and open flexible structures perforated by voids at high pHs. The voids can trap and adsorb both organic and inorganic particles if the charges are complementary.

## **Project Description**

This project is underway to develop HUMASORB-CS™ to remove in one processing step, heavy metal and organic contaminants from groundwater and surface waters found at typical DOE and industrial sites. The development of HUMASORB™ is divided into two phases. Phase I-- isolation, purification, and evaluation of humic acid, preparation and preliminary characterization of HUMASORB-CS™, was successfully completed and was a significant milestone and a major decision point. Under the Phase II activities, that began in April 1996, HUMASORB-CS™ was successfully cross-linked and immobilized. The new material is currently undergoing bench- and pilot-scale column tests. The various tasks in Phase I included:

- isolation and purification of humic acid
- characterization of contaminant removal
- cross-linking humic acid to form HUMASORB-CS™
- evaluation of HUMASORB-CS™ for contaminant removal

The tasks in Phase II include:

- immobilization of HUMASORB-CS<sup>TM</sup> to improve handling properties and lower solubility
- evaluation of immobilized HUMASORB-CS<sup>TM</sup> in batch and column studies
- stability studies on HUMASORB-CS<sup>TM</sup>
- conceptual process design and economic analysis.

The procedure for the experiments used to determine contaminant removal in batch mode are presented elsewhere (1). A similar procedure was used for the experiments from which the results are presented here. The humic acid based adsorbents used in this project include:

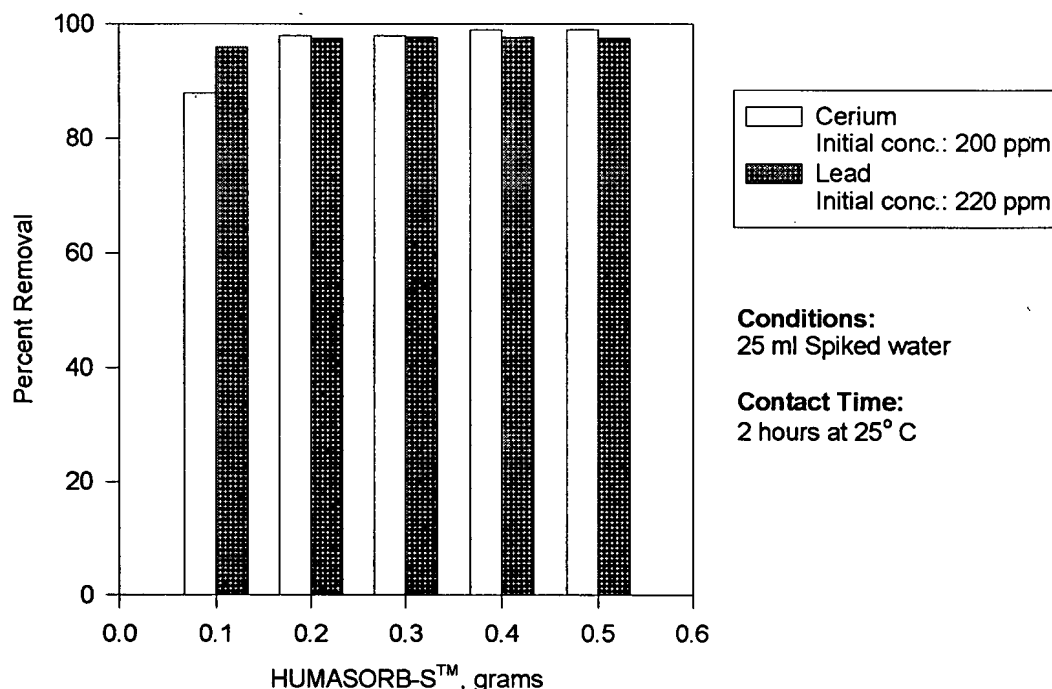
- liquid humic acid termed HUMASORB-L<sup>TM</sup>
- purified humic acid termed HUMASORB-S<sup>TM</sup>
- cross-linked humic acid obtained from either HUMASORB-L<sup>TM</sup> or HUMASORB-S<sup>TM</sup> termed HUMASORB-CS<sup>TM</sup>

## Results

The effectiveness of HUMASORB<sup>TM</sup> for removal of different metals, organics and representative radionuclides was presented earlier (1). The metal-sorption data was analyzed using the method developed by Scatchard (2). The presence of more than one inflection point on a plot based on Scatchard analysis usually indicates the presence of more than one type of binding site. Scatchard analysis of the results from the experiments in this study indicated the possibility of more than one type of binding site for copper and nickel sorption. The plot was however, linear for cadmium indicating that possibly only one type of binding site was active for cadmium sorption (1).

The effect of HUMASORB-S<sup>TM</sup> loading on removal of lead and cerium (a surrogate for plutonium) from simulated waste streams is shown in Figure 1. The results indicate that HUMASORB<sup>TM</sup> has high affinity for both lead and cerium. The mechanism for contaminant removal is believed to be a combination of ion-exchange and chelation/complexation. The results presented in Figure 1 are with simulated waste streams containing only one contaminant. The effect of multiple contaminants on HUMASORB-S<sup>TM</sup> performance was evaluated using a simulated waste stream containing copper, chromium and lead and treating it with HUMASORB-S<sup>TM</sup> at different loadings. The effect of contact time was also evaluated by reacting for two hours and 24 hours. The results indicate a relatively higher affinity for lead and copper removal compared to that for chromium (Figure 2). In addition, increased contact time did not have any significant effect on the removal of lead and copper. However, the removal of chromium increased with longer contact time and chromium removal was relatively lower compared to lead

Figure 1. HUMASORB-S™ is Effective for Metal Removal



and copper for a given adsorbent loading. This indicates that the removal of chromium could be the rate limiting step under the conditions of this study.

HUMASORB-S™ is insoluble in water at lower pH, but could dissolve at higher pH in the presence of monovalent metals ions such as sodium and potassium. A cross-linked humic acid polymer--HUMASORB-CS™ was produced to overcome this limitation and lower the solubility at higher pHs. HUMASORB-CS™ was produced by cross-linking HUMASORB-S/L™ using different proprietary methods. The solubility of the cross-linked product was determined at various pH and compared with humic acid. The results shown in Figure 3 indicate that the solubility of HUMASORB-CS™, as determined under the conditions of this study, is significantly lower compared to that of humic acid. The different functional groups present in HUMASORB™ before and after cross-linking were estimated using <sup>13</sup>C-NMR and are shown in Table 1. The analysis indicates that all the functional groups, that are believed to be responsible for contaminant removal, are retained after cross-linking.

The ability of HUMASORB-CS™ to remove different contaminants was evaluated and compared with removal before cross-linking. The results from simulated streams containing single contaminants such as chromium, strontium (Figures 4 & 5) and streams containing multiple contaminants such as copper, chromium and lead (Figure 6) indicate that the contaminant removal properties of humic acid are retained in HUMASORB-CS™ and in a few cases enhanced after

cross-linking. In addition, the results with a stream containing multiple contaminants, indicate that chromium removal is the rate limiting step and required higher loading of the adsorbent. This is similar to the performance of HUMASORB™ before cross-linking.

Figure 2. HUMASORB-S™ is Effective for Metal Removal from Simulated Waste Streams Containing Multiple Contaminants

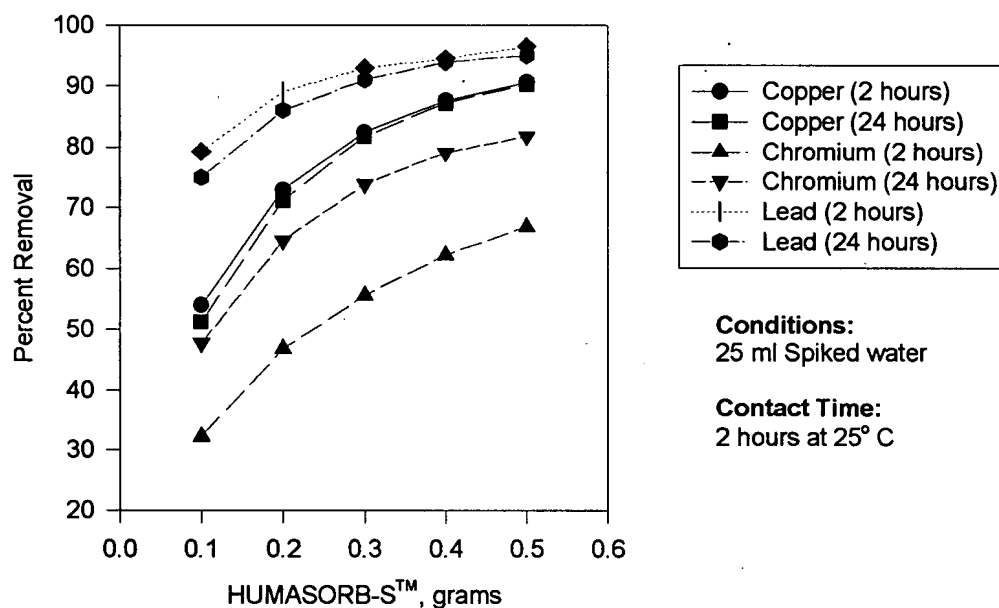


Table 1

FUNCTIONAL GROUP COMPOSITION OF DIFFERENT HUMASORB-CS™ PRODUCTS  
(ESTIMATED FROM SOLID STATE <sup>13</sup>C-NMR SPECTROSCOPY)

SAMPLE	Paraffinic carbon, amines %	Carbohydrates, alcohols %	Aromatic carbon %	Carboxyl %
HUMASORB-L™ (dried)	8.84	15.01	57.96	18.14
HUMASORB-S™	21.94	23.75	37.03	17.24
HUMASORB-CS™ (enzymatically)	26.39	21.87	33.58	18.11
HUMASORB-CS™ (chemically)	22.98	26.22	34.05	16.69

Figure 3: HUMASORB-CS™ Solubility is Lower After Cross-Linking and Immobilization

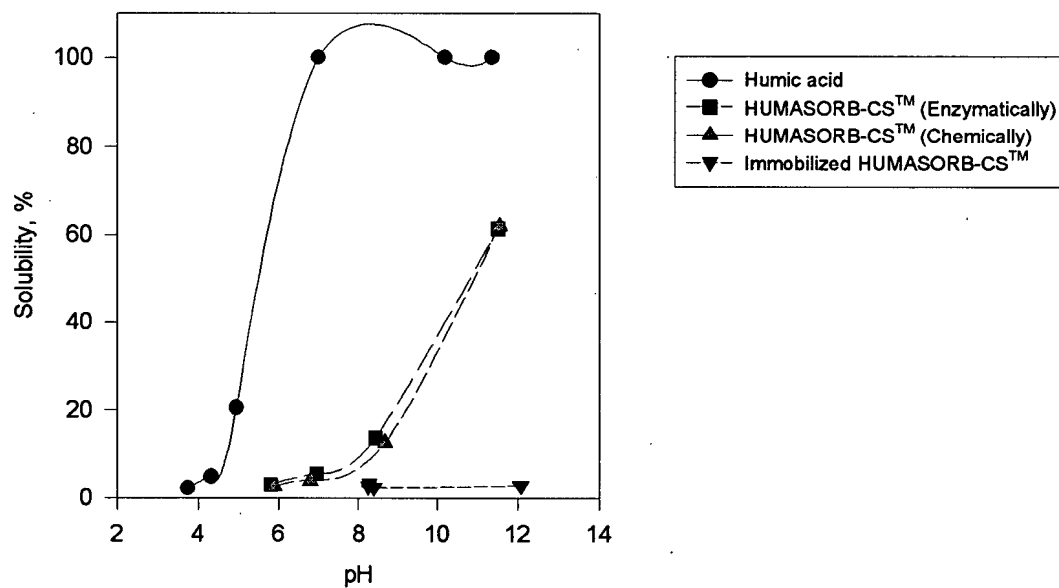


Figure 4: Chromium (III) Removal is Significantly Enhanced by HUMASORB-CS™

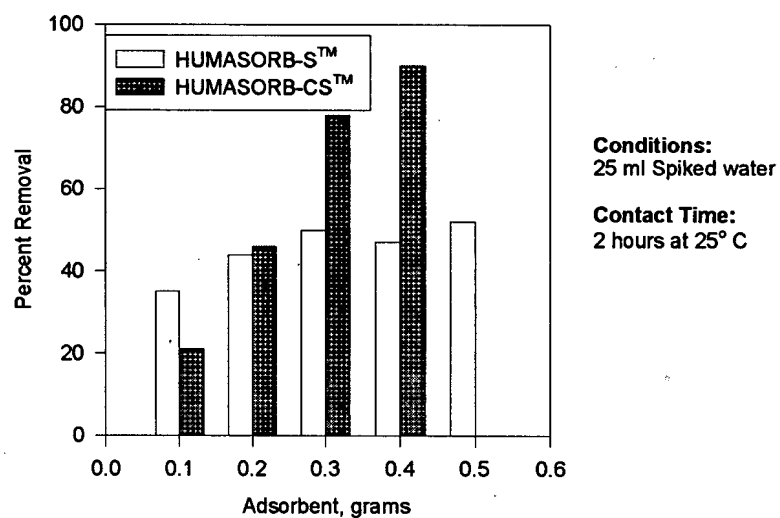




Figure 5: HUMASORB-CS™ Enhances Strontium Removal

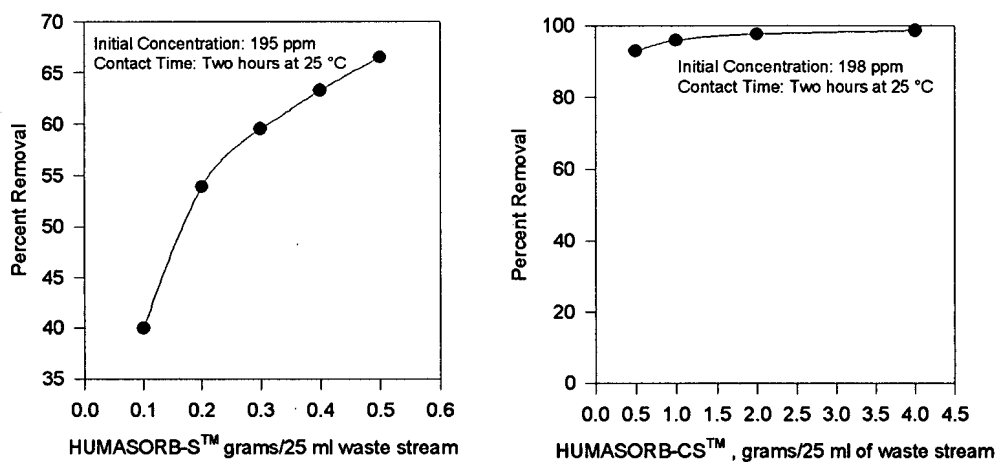
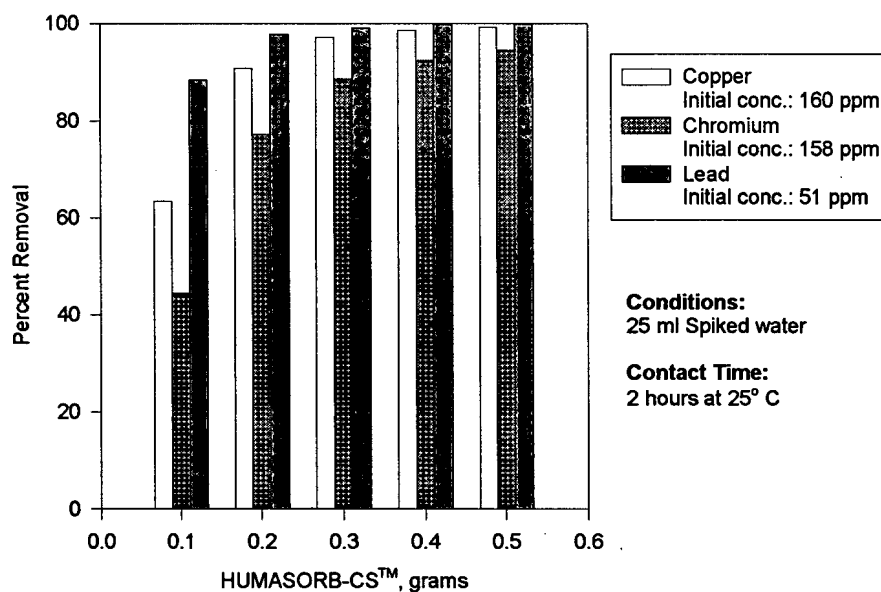


Figure 6: Multiple Toxic Metal Removal from Spiked Water by HUMASORB™



The results from some of the experiments conducted as part of this project were used to determine the distribution coefficients. The coefficient  $K_d$  is defined as

$$K_d = C_s / C_l$$

where,  $C_s$  is the concentration of the contaminant in the solid phase and  $C_l$  is the concentration in the liquid phase.

Distribution coefficients for various contaminants are listed in Tables 2 & 3. The distribution coefficient was determined from batch isotherm studies, in which different amounts of the adsorbent were contacted with simulated waste streams. The table indicates that HUMASORB-S™ has very high affinity for uranium, and is also very effective in removing different metals from simulated waste streams.

The data presented in Tables 2 & 3 indicate that HUMASORB™ had higher distribution coefficients after cross-linking. The higher distribution coefficients with HUMASORB-CS™ at comparatively lower equilibrium concentration indicates that cross-linking has enhanced metal removal from contaminated water. Higher distribution coefficients with HUMASORB-CS™ for different metals is also evident in batch adsorption studies with contaminated streams containing multiple metals as shown in Table 3.

Table 2: HUMASORB-CS™ Enhances Strontium and Chromium Distribution Coefficients

CONTAMINANT	EQUILIBRIUM CONCENTRATION IN THE LIQUID PHASE, ppm	DISTRIBUTION COEFFICIENT*, $K_d$ , ml/gm	pH
WITH HUMASORB-S™			
Uranium	0.01	> 100,000	5.1
Lead	5	3500	2.25
Cerium	1.7	5600	2.5
Strontium	65.3	99	2.2
Chromium	138	54	3.2
WITH HUMASORB-CS™			
Strontium	2.87	430	5.1
Chromium	22.65	566	3.2

\*: As determined from batch isotherm studies with only one contaminant present in the system.

**Column Studies:** HUMASORB-CS™ is now being used in bench-scale columns in continuous mode. In these studies, simulated waste streams containing various contaminants are passed through a column packed with HUMASORB-CS™ or a mixture of sand and HUMASORB-CS™. The empty bed contact time (EBCT) in most of the studies conducted to date range from one to four minutes. In one of the experiments, EBCT was approximately 13 minutes. The bed volumes treated at breakthrough depends on the contaminant and its concentration in the input stream to the column. In one of the column studies, breakthrough was not attained even after 2500 bed volumes based on HUMASORB-CS™ loading in the column. A detailed analysis of the results from the column studies conducted to date is underway at present. The spent HUMASORB-CS™ from the column studies was regenerated by traditional techniques used to regenerate ion-exchange resins. The results show that HUMASORB-CS™ could be regenerated for at least one or two cycles.

Table 3: HUMASORB-CS™ Enhances Copper, Chromium, and Lead Distribution Coefficients

CONTAMINANT	EQUILIBRIUM CONCENTRATION IN THE LIQUID PHASE, ppm	DISTRIBUTION COEFFICIENT*, $K_d$ , ml/gm	pH
WITH HUMASORB-S™			
Copper	6.8	666	2.2
Chromium	14	260	2.2
Lead	2	450	2.2
WITH HUMASORB-CS™			
Copper	<0.5	11,870	4.0
Chromium	< 0.5	8514	4.0
Lead	< 0.5	1700	4.0

\*: As determined from batch isotherm studies with three inorganic and two organic contaminants present in the system.

## Future work

HUMASORB-CS™ developed in this study will be used in column studies using various representative contaminants. The types of contaminants to be evaluated during Phase II of this project include metal ions, radionuclides or surrogates, oxo-anions, chlorinated and fuel hydrocarbons. The future work in this project includes:

- evaluation of contaminant removal in columns packed with HUMASORB-CS™,
- evaluate stability of HUMASORB-CS™ in water at different temperatures, and in the presence of ions such as carbonate, sulfate,
- conceptual design and economic analysis.

## Applications/Benefits

The remediation of contaminated streams and groundwater has been traditionally approached with at least a two-step process including some combination of activated carbon and ion-exchange process. HUMASORB-CS™, derived from a naturally occurring material has the potential to alleviate some of the limitations of multi-step processing by combining remediation efforts into a single step process. The use of a single-step process for remediation systems could reduce the cost of clean-up of various contaminated streams and groundwater at a number of DOE facilities. HUMASORB-CS™ can be used for groundwater clean-up both in the in-situ mode and in a pump and treat process. The benefits of HUMASORB-CS™ use include:

- Improved process performance due to enhanced contaminant removal by HUMASORB-CS™

- Reduced unit operations obviating the need for multiple process units
- Reduced complexity of metal-recovery and waste disposal when needed.

### **Acknowledgments**

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### **References**

1. Sanjay, H.G., et al. In Proceedings of the Environmental Technology Through Industry Partnership Conference, October 1995, DOE/METC-96/1021, Vol. 2.
2. Scatchard, G. The attraction of proteins for small molecules and ions, Ann. New York Acad. Sci., 51, 660-672, 1949.